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Geochemistry of Fe³⁺ in the hydrothermal dickite from Jedlina Zdroj (Lower Silesia, Poland)

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Abstract: Geochemical analysis for Fe was made on a representative sample of dickite-rich hydrothermal clay from Jedlina Zdroj. The mineralogy of the sample is comparatively simple, dickite being the principal component (>95 wt. % of the total sample), with lesser amounts of goethite and barite. Geochemical fractionation and inductively coupled plasma–optical emission spectrometry indicated that most of the Fe (*ca.* 97 wt. % of the total metal) resides in the dickite. Electron spin resonance showed that some of the Fe in the dickite structure is in the form of Fe³⁺. A substantial proportion of these ions (as well as Fe) in the dickite matrix were probably contained in the original hydrothermal dickite-forming solution. From the geochemistry of Fe³⁺, it was deduced that the oxidation potential (*Eh*) and pH of the solution during the formation of dickite from the Jedlina Zdroj were approximately 0.45–0.95 V (highly oxygenated) and 0–4 (highly acidic), respectively.

Keywords: kaolinite; dickite; iron.

INTRODUCTION

The kaolinite group of minerals includes kaolinite, dickite, nacrite and halloysite. Kaolinite minerals are widespread in crustal rocks, particularly where there hydrothermal acid waters flow existed.¹ Hydrothermal dickites were mainly formed *in situ* through alteration of source minerals (mainly potassium-rich feldspars and other Al-rich silicates) by hydrothermal acid waters.^{2,3} In Lower Silesia, hydrothermal dickite has been recognized for a long time and was named “pholerite” by researchers (*e.g.*, Kowalski and Lipiarski).⁴ The Polish literature concerning hydrothermal dickite in Lower Silesia is, however, relatively scarce and this type of clay minerals is generally considered rare.^{4,5} This report is a part

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of a larger study that attempts to evaluate the nature and origin of hydrothermal dickite in volcanic rocks recovered from Lower Silesia.

In recent years, considerable attention has been given to the genesis of dickite in sedimentary conditions. However, its origin and genesis is still a matter of debate. Dickite is generally considered to be a relatively high-temperature polymorph, although many other occurrences have been reported in hydrothermal and diagenetic environments, indicating that the genetic conditions are less restrictive than were initially envisaged.

Geochemical studies indicate that iron occurs in natural aquatic environments in two oxidation states, Fe(III) and Fe(II). In low (suboxic/anoxic) *Eh* natural environments, the main aqueous Fe(II) species are Fe^{2+} and $\text{Fe}(\text{OH})^+$. In oxygenated (aerated) natural waters, Fe is predicted to occur in the +3 oxidation state, primarily as highly soluble and mobile ions. These ions have a strong tendency to interact with the surface of Al and other metal hydrous oxides and are thus capable of becoming specifically bound within colloidal clay particles.

Physicochemical conditions during the formation of non-hydrothermal kaolinites are usually deduced from field data as well as experimental/thermodynamic data. The stability of these mineral is often expressed in plots using pH and ion activities. The hydrothermal kaolinites/dickites are not frequently studied and knowledge of the physicochemical conditions necessary for their formation is still obscure.

One way to obtain an objective evaluation of the nature of a solution during the formation (precipitation) of hydrothermal dickite (or kaolinite) is to examine components that undoubtedly were introduced into its lattice by this solution. Such a component is, for certain, Fe^{3+} . On the other hand, chemical conversions of Fe^{3+} into Fe^{2+} in natural aquatic environments are characterized almost entirely by the pH and oxidation reduction potential (*Eh*) of the environment. These two parameters also have a strong influence on the mobility and complexation of Fe^{3+} . Thus, Fe^{3+} is a sensitive geochemical indicator of the geochemistry of dickite-forming waters and it may provide clues to the origin of hydrothermal clay deposits of the past. These facts led us to study Fe^{3+} in a well-ordered dickite, a hydrothermal mineral enriched with Fe, in a dickite-rich sample from Jedlina Zdroj. In addition, selective leaching procedures were used to establish geochemical associations and specific mineralogical residences for Fe and Fe^{3+} in this clay. As far as we are aware, this is the first time that this approach has been employed to describe the physicochemical conditions of formation of any clay mineral.

EXPERIMENTAL

Sample location and description

Jedlina Zdroj is a town situated in Lower Silesia (southwestern Poland) in the region of Walbrzych, the Sudetes Basin. The geographical location of the Jedlina Basin is shown in Fig. 1.



Fig. 1. Geographical location of Jedlina Zdroj and Nowa Ruda.

The blue-green dickite-rich clay at Jedlina Zdroj occurs mainly as veins of hydrothermal origin within volcanic (rhyolitic) rocks. This clay occurs also as small white nodules in late Paleozoic volcanic rocks.⁵ A set of 11 samples were collected from the outcrop site at Jedlina Zdroj, in which dickite-rich veins are abundant; dickite is primarily associated with dark-grey kaolinitic shales, Fig. 2. Sub-samples were hand picked for analysis in order to minimize the inclusion of impurities. The present detailed study of dickite was performed on one of these



Fig. 2. Example of blue-green dickite filling the veins within black shales/slates from Jedlina Zdroj. Sample size: ca. 12×11 cm.

subsamples (hereafter JDS), which contained predominantly dickite. Powdered samples for analyses were obtained by scraping the dickite-rich clay surface with a razor blade.

Dickite-rich clay is also found throughout the abandoned coal mine Piast near the town of Nowa Ruda (about 20 km from Jedlina Zdroj, Fig. 1). According to Kowalski and Lipiarski,⁴ dickite from Jedlina Zdroj and Nowa Ruda may have originated in hydrothermal solutions genetically related to the magmatism of the Late Carboniferous.

Analytical methods

Chemical analysis. Chemical analyses were realized using standard methods for silica and alumina, and colorimetric methods for Fe and Ti.

Inductively coupled plasma–optical emission spectroscopy (ICP–OES) analysis. The Fe contents of the various fractions of JDS (see below) were analyzed by a Spectroflame ICP–OES instrument using Ar as the plasma gas.

X-Ray diffraction (XRD) analysis. XRD Patterns were obtained with a Philips PW 1729 vertical goniometer using CoK α radiation (35 kV, 30 mA). Powder diffractograms were acquired in the 3–90° 2θ range, with 7–20 s counting per 0.04° 2θ step. The samples were prepared using the back-loading procedure according to Moore and Reynolds,⁶ which provides significant disorientation of the clay layers.

Fourier transform infrared (FTIR) spectrometry. FTIR Spectra were recorded in the absorbance mode using a BOMEM Michelson Series MB FTIR spectrometer set to give undeformed spectra. The resolution was 4 cm⁻¹ in the 400–4000 cm⁻¹ analyzed range. The spectra were obtained at room temperature from KBr pressed pellets prepared by mixing 1.5 mg of a dickite fraction (see below) sample with 150 mg of KBr.

Scanning electron microscopy (SEM)/energy-dispersive spectrometry (EDS). The morphology and the semi-quantitative chemical analyses of polished thin sections of JDS-s were performed by scanning electron microscopy (SEM; Philips XL 30 ESEM/TMP scanning microscope) coupled to an energy-dispersive spectrometer (EDAX type Sapphire). The analytical conditions were as follows: accelerating voltage 15 or 25 kV, probe current 60 nA, working distance 25 mm and counting time 100 s. The individual parameters are printed on the microphotographs: acceleration of electron beam, magnification, type of detector: SE (secondary electrons), CEN (BSE-backscattered electrons). The samples were coated with gold.

Electron spin resonance (ESR) spectrometry. The ESR measurements were performed on finely-ground powders of the dickite samples that were transferred to an ESR quartz tube. The spectra were recorded on a Bruker ESP 300E spectrometer at X-band (9.4 GHz) using standard 100 kHz field modulation. The spectra were recorded at room temperature. Additional experimental parameters were as follows: 100 mW microwave power and 1 mT modulation amplitude. The ESR spectra were recorded in the 0 to 6 mT magnetic field range.

Analysis and fractionation

The fractionation procedure was similar to that used by Premović.⁷ The flow chart in Fig. 3 outlines the major steps in preparing the four fractions of JDS.

Thus, powdered rock (1 g) was treated (room temperature, 12 h) with acetate buffer (acetic acid/sodium acetate, 1 M, pH 5.0) to remove most of the carbonates. The soluble material constitutes the carbonate fraction. Carbonate removal was checked by FTIR/EDS analyses.

The insoluble residue (I) was demineralized further by repeated treatment with cold HCl (6 M). This acid solution removed mostly metal oxides, including Fe oxides. The soluble part constitutes the cold HCl-fraction.

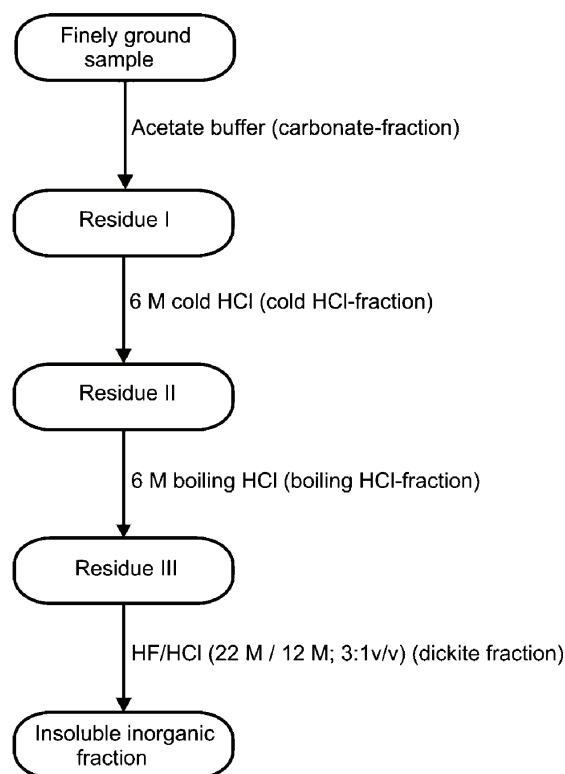


Fig. 3. Flow chart of the fractionation procedure.

The insoluble residue (II) was demineralized with boiling HCl (6 M, 80 °C, 12 h). This treatment removed most of the soluble silicates. The soluble part constitutes the boiling HCl-fraction.

The insoluble residue (III) was demineralized with boiling hydrofluoric acid HF/HCl (22 and 12 M, 3:1 v/v, respectively, 80 °C, 12 h). This acid mixture removes SiO₂ and Al₂O₃. The removal of SiO₂ and Al₂O₃ was checked by FTIR/EDS analyses. The soluble part constitutes the dickite fraction or phase.

The residue from (III) is the acid insoluble fraction.

RESULTS

Chemical and ICP–OES analyses

The acetate buffer/HCl demineralization steps removed only 9 wt. % of JDS. The mass loss was due to the total dissolution of carbonates (acetate buffer: 2 wt. %), the dissolution of metal oxides, including Fe-oxides (cold-HCl: 5 wt. %) and the destruction of some silicate minerals (boiling HCl: 2 wt. %), Table I. SiO₂ and Al₂O₃, the dominant constituents of JDS, seem to have been unaffected by the demineralization steps. Geochemical analysis also indicated that more than 91.5 wt. % of the dickite fraction was removed by the HF/HCl step. Chemical

analysis showed that the major components were 43.3 wt. % SiO₂, 40.0 wt. % Al₂O₃, 1.5 wt % TiO₂ and 1.0 wt. % Fe₂O₃.

The distribution of Fe among the four components of JDS is given in Table I, which shows that Fe was relatively abundant (2130 ppm) in JDS and that about 97 wt. % of this metal was associated with the dickite phase. A survey of the literature showed that the total Fe content in hydrothermal dickites was about 1 wt. %.

TABLE I. Geochemical distribution of Fe (ppm) from selective leaching experiments of JDS

Fraction	Sediment (± 5 wt. %)	Fe
Acetate buffer	2.0	$\leq 1^a$
Cold-HCl	5.0	3750
Boiling-HCl	2.0	5200
Dickite	91.5	1900
Insoluble residue	0.0	—
Total sample ^b	100.5	2130

^aDetection limit of the ICP-OES employed; ^bthe total Fe content obtained by summation of the Fe concentrations determined in the fractions by ICP-OES

FTIR Analyses

An accurate distinction between kaolinite and dickite can be achieved employing FTIR spectroscopy, by assessing the position and relative intensity of the OH-stretching bands in the 3600–3700 cm⁻¹ region of an IR spectrum.⁸ The FTIR spectrum of the dickite fraction of JDS, which is characteristic for dickite, is shown in Fig. 4a and, for comparison, the FTIR spectrum of a KGa-1 reference sample is given in Fig. 4b. The KGa-1 sample exhibited a strong absorption at 3697 cm⁻¹, a band of medium-strong intensity at 3620 cm⁻¹ and two relatively weak absorptions at 3669 and 3652 cm⁻¹. On the other hand, the dickite sample showed a strong absorption at 3621 cm⁻¹ and two medium-strong absorption bands at 3704 and 3654 cm⁻¹.

XRD Analyses

The XRD pattern of powdered JDS is shown in Fig. 5. The bulk samples showed dickite as the predominant mineral.

SEM/EDS Examination

The SEM results showed that the dickite phase of JDS had the morphology of well-formed, uniform aggregates of dickite particles (Fig. 6). EDS Analyses showed that this mineral mainly consists of O, Al and Si (Fig. 7a); minor amounts of K, Fe and Ti were also detected. In addition, the presence of minor amounts of goethite (Fig. 7b) and barite (Fig. 7c) was evidenced in JDS by the combined use of SEM/semi-quantitative chemical analysis of EDS. Apparently, dickite and goethite, (α -(FeO(OH))), precipitated simultaneously in JDS.

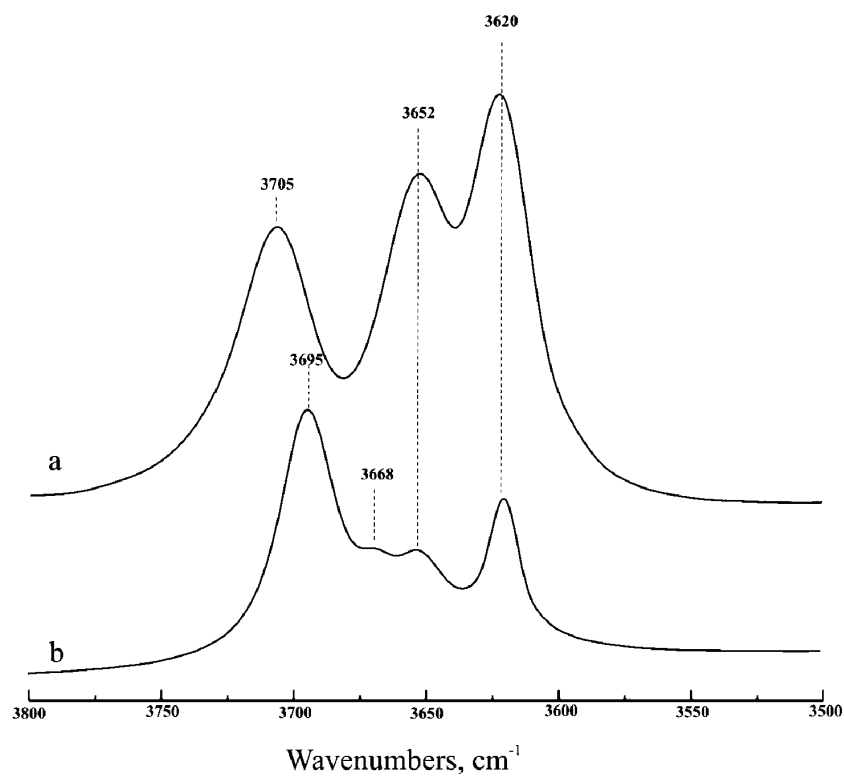


Fig. 4. FTIR Spectra in the OH stretching vibrations region of a) the dickite fraction of JDS Zdroj and b) KGa-1 (a reference kaolinite).

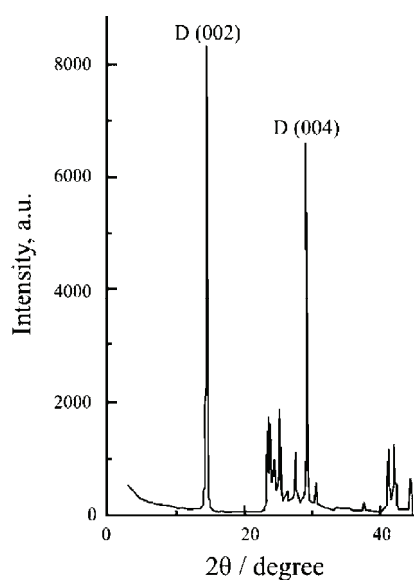


Fig. 5. X-Ray diffraction pattern of JDS. Diagnostic peaks of dickite are marked with D.

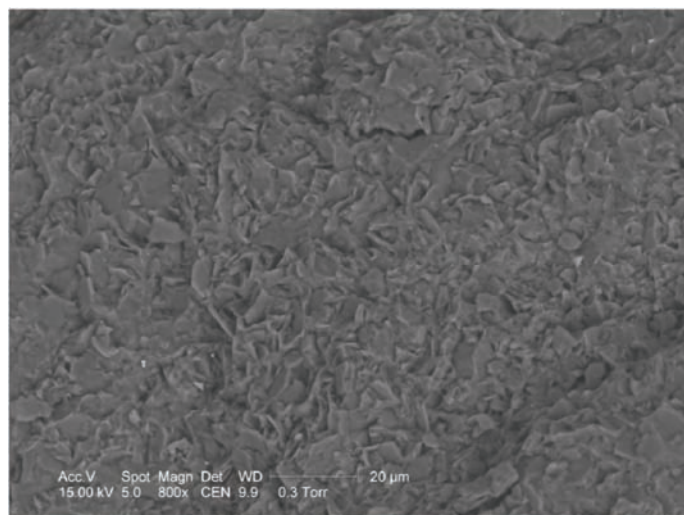


Fig. 6. Scanning electron micrographs of bulk JDS.

ESR Analyses

Untreated JDS showed only a complex ESR signal around $g = 4$ and a sharp isotropic ESR signal around $g \approx 2$, superimposed on a broader one (Fig. 8). The high g -pattern of JDS was often found for isolated Fe^{3+} in the structure of well-ordered kaolinites (*e.g.*, KGa-1), substituting for Al^{3+} in the octahedral sheets.⁹ The Fe^{3+} signals of JDS remained after chemical treatment with cold/boiling HCl, but they disappeared after treatment with HF/HCl solution. This means that Fe^{3+} are probably within the structure of the host dickite. The sharp ESR signal at around $g \approx 2$ is characteristic for a relatively stable paramagnetic defect within the structure of dickite.

DISCUSSION

The oxygenated dickite-forming solution

Kraynov and Ryzhenko,¹⁰ who made a thorough study of the Eh/pH values in many geochemical water types, reported that the acidity of hydrothermal acid waters (in areas of contemporary magmatism) is within the pH range of *ca.* 0–4 and the Eh values vary from 0.6–0.9 V. The field of these waters in Fig. 9 is presented by the shaded area.

The fact that *ca.* 97 wt. % of the Fe of JDS (Table 1) resides within the dickite structure indicates that some of the Fe in the dickite-forming hydrothermal solution was in a dissolved form. It is suggested that most of this metal was introduced into the dickite by this solution already enriched in Fe. This process occurred during mineral formation but not afterwards.

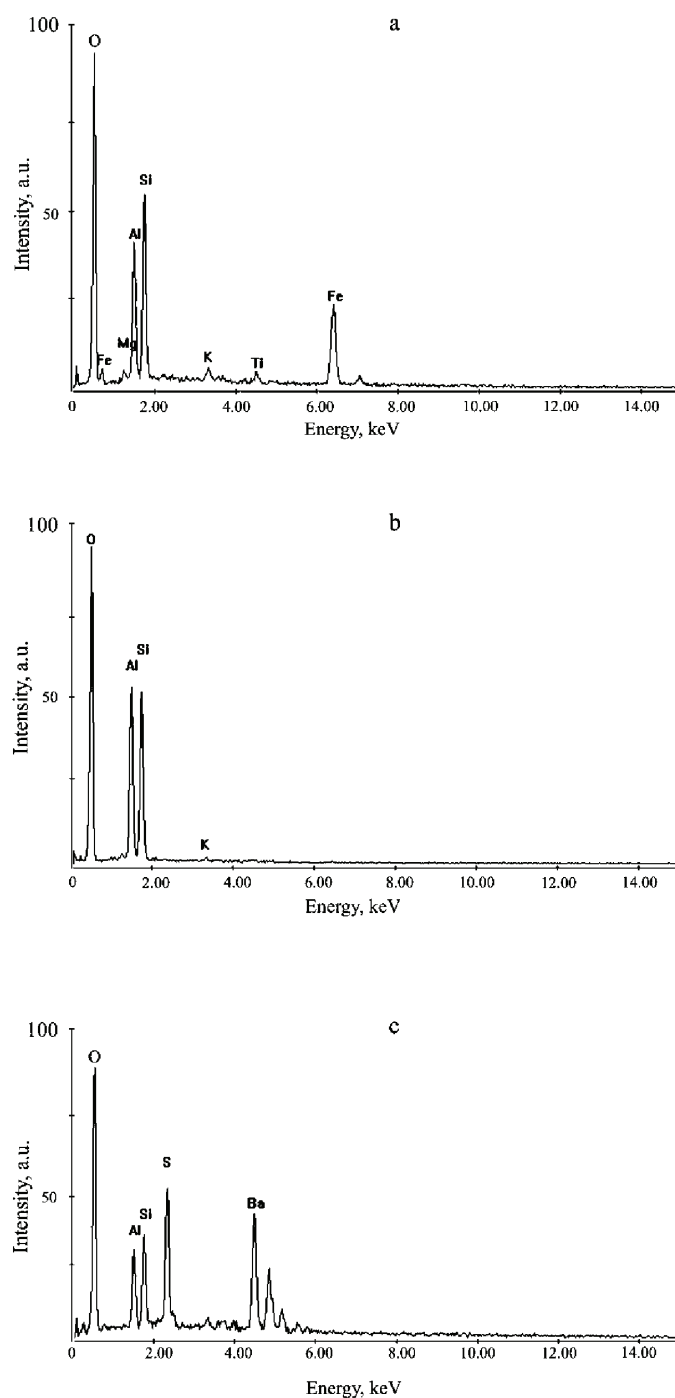


Fig. 7. EDS Analyses of the (a) dickite, (b) goethite and (c) barite in JDS.

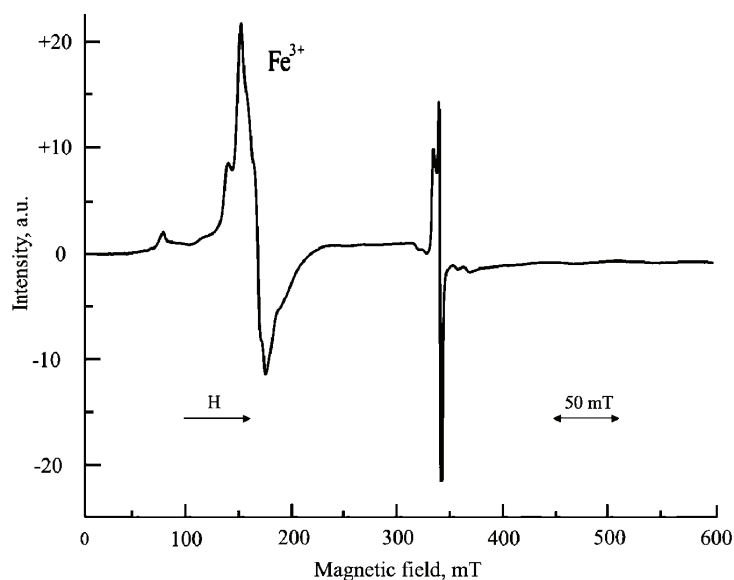


Fig. 8. The ESR spectrum of untreated JDS with Fe^{3+} within the dickite structure.

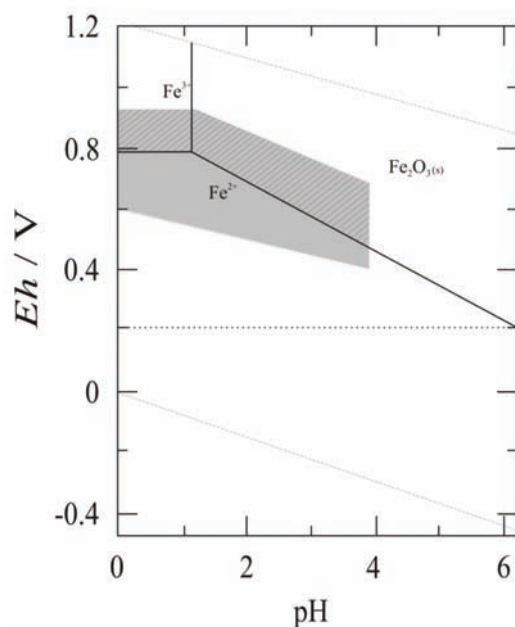


Fig. 9. *Eh*-*pH* diagrams for Fe^{3+} at 300 K and 1 atm of the forming solution (enriched with Fe^{3+}) of the dickite from Jedlina Zdroj. The assumed total Fe concentration was 200 ppm. The shaded area represents the *Eh/pH* region of hydrothermal waters defined by Kraynov and Ryzenko.¹⁰ The probable physicochemical conditions of the dickite from Jedlina Zdroj are represented by the dashed area.

The ESR investigation showed that a high amount of the Fe^{3+} are incorporated into the structure of dickite. This indicates that these ions were present in relatively high concentrations in the precipitating solution at the time when this mineral was formed. It is also reasonable to suggest that this solution was oxy-

generated. Indeed, under anoxic conditions, Fe would precipitate mainly as pyrite (FeS_2), as both Fe^{2+} and Fe^{3+} are unstable with respect to pyrite in anoxic aquatic environments.¹¹

The presence of authigenic goethite associated with JDS (Fig. 7b) is consistent with its formation occurring under highly oxygenated conditions, as goethite occurs only in a natural aqueous milieu under these conditions, with an *Eh* value above 0.15 V.¹² Note that formation of goethite and other Fe-hydroxides becomes predominant at $\text{pH} > 3$.¹¹

Source of Fe

In general, all hydrothermal waters are brines and Fe is commonly present at levels of up to a few tens or hundreds ppm. The source(s) of this metal in a hydrothermal water can rarely, if ever, be identified with certainty.¹³ Waters within a shallow-water hydrothermal system (such as Jedlina Zdroj) may be derived from any one or combination of the following sources: meteoric and juvenile (connate and magmatic) waters (*e.g.*, Nicholson¹⁴). On-land hydrothermal systems derive most of their waters from meteoric sources along with possible magmatic contributions (*e.g.*, Giggenbach¹⁵). A survey of the literature showed the magmatic waters usually contain very high concentrations of dissolved Fe (>1000 ppm). In contrast, meteoric waters are usually Fe-poor (about 10 ppm or so). Thus, it is speculated that the dickite-forming hydrothermal solution at Jedlina Zdroj was probably generated by the mixing of ascending magmatic Fe-rich waters and oxygenated Fe-poor meteoric water.

Eh–pH diagram

Employing the FactSage thermochemical software/Fact compound databases, stability diagrams of Fe^{3+} for physicochemical conditions close to natural hydrothermal conditions as defined by Kraynov and Ryzhenko¹⁰ were constructed, Fig. 9. For the sake of simplicity, only a part of the diagram is shown. A total Fe concentration of 200 ppm was assumed in this construction. The critical boundary between the stability fields of Fe^{3+} is not significantly affected by modifying this value even 10-fold in either direction.

It is apparent from Fig. 9 that the Fe^{3+} is only thermodynamically stable under oxic conditions (*Eh* from 0.45 to 0.95 V) and at low pH values (0–4); accordingly, the relatively high concentration of Fe^{3+} within the dickite from Jedlina Zdroj is only consistent with a highly acidic (pH 0–4) and oxygenated (*Eh ca.* 0.45–0.95 V) dickite-forming solution. The above *Eh*–pH diagram was calculated for atmospheric pressure and a temperature of 25 °C. A thermochemical calculation indicated that no significant variations in the thermodynamic parameters on the scale of the diagram are to be expected up to a pressure of 10 bar. This is because pressure affects only slightly the chemistry of both ionic spe-

cies and solids of Fe within the O–H geochemical system. A similar calculation also showed that in a dickite-forming solution with temperatures reaching up to *ca.* 150 °C, the vertical line which represents the boundary between Fe³⁺ and Fe₂O₃ would be shifted only slightly.

Of course, the *Eh*–pH diagram presented in Fig. 9 it is not an accurate representation of the dickite-forming solution and it undoubtedly is highly variable in its approach to ideal. Yet, because it represents a quantitative estimate based on the available thermodynamic data, it should be a helpful tool, if used within its limitations.

CONCLUSIONS

Examination of a representative dickite-rich sample from Jedlina Zdroj by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray and Fourier transform infrared analyses showed that dickite predominates with associated minor quantities of goethite and barite. Geochemical analysis showed a relatively high concentration of dissolved Fe which was present in the precipitating solution at the time when this hydrothermal mineral was formed. The abundant presence of Fe³⁺ (detected by ESR spectroscopy) within the dickite structure and the associated authigenic goethite indicates that this solution was highly oxygenated with an oxidation potential *Eh* and pH of *ca.* 0.45–0.95 V and 0–4, respectively.

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ИЗВОД

ГЕОХЕМИЈА Fe У ХИДРОТЕРМАЛНОМ ДИКИТУ ИЗ ЈЕДЛИНЕ ЗДРОЈ (ДОЊА ШЛЕЗИЈА, ПОЉСКА)

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Урађена је геохемијска анализа Fe на репрезентативном узорку хидротермалне глинe богате дикитом са локације Једлина Здрој. Минералогија узорка је веома једноставна. Дикит је основна компонента (>95 % од целокупног узорка), са мањим количинама гетита и барита. Геохемијска фракцинација и индуктивно спрегнута плазма–оптичко емисиона спектрометрија показују да је највећи део Fe (око 97 % од присутног метала) уграђен у структуру дикита. Електронспинска резонанција показује да се део Fe у структури дикита налази у облику Fe³⁺. Значајан део Fe³⁺ (као и Fe) у дикитној структури се, вероватно, налази у првобитном хидротермалном раствору из кога се формирао дикит. На основу геохемије Fe³⁺ закљу-

чено је да су оксидациони потенцијал (Eh) и pH раствора за време формирања хидротермалног дикита са локације Једлина Здрој у опсегу 0,45–0,95 V (изразито оксидациони) и 0–4 (изразито кисело).

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REFERENCES

1. G. Izquierdo, V. M. Arellano, A. Aragón, E. Portugal, I. Martinez, in *Proceedings of the World Geothermal Congress*, (2000), Kyushu – Tohoku, Japan, (2000), p. 1301
2. H. H. Murray, W. Bundy, C. Harvey, *Kaolin genesis and utilization*, The Clay Minerals Society, Special Publication 1, Clothbound, 1993
3. N. Malengreau, J.-P. Muller, G. Calas, *Clays Clay Miner.* **42** (1994) 137
4. W. M. Kowalski, I. Lipiarski, *Geol. T.* **78** (1973) 7
5. K. Lydka, *Arch. Mineral.* **26** (1966) 501
6. D. M. Moore, R. C. Reynolds Jr., in *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, D. M. Moore Jr., R. C. Reynolds, Eds., Oxford University Press, Oxford and New York, 1989, p. 179
7. P. I. Premović, *Geochim. Cosmochim. Acta* **48** (1984) 873
8. J. D. Russell, in *Infrared methods*, M. J. Wilson, Ed., Blackie, Glasgow, 1987, p. 133
9. J. M. Gaite, P. Ermakoff, J. P. Muller, *Phys. Chem. Minerals* **20** (1993) 242
10. S. R. Kraynov, B. N. Ryzhenko, *Geochem. Int.* **29** (1992) 1
11. R. M. Garrels, C. L. Christ, *Solutions, Minerals and Equilibria*, Harper and Row, New York, 1965, p. 453
12. W. C. Krumbein, R. M. Garrels, *J. Geol.* **60** (1952) 1
13. *Geochemistry of Hydrothermal Ore Deposits*, 3rd ed., H. L. Barnes, Ed., Wiley, 1997
14. K. Nicholson, *Geothermal Fluids*, Springer-Verlag, Heidelberg, 1992, p. 266
15. W. F. Giggenbach, *Econ.Geol.* **87**(1992) 1927.